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THE REDOX CHEMISTRY OF SOME PEROXO AND SUPEROXO METAL
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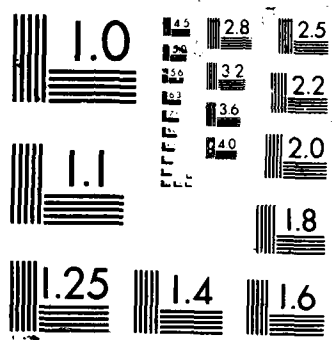
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THE REDOX CHEMISTRY OF SOME PEROXO AND SUPEROXO
METAL ION COMPLEXES



FINAL REPORT

Richard C. Thompson

November 3, 1987

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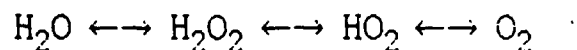


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Statement of Work

The mechanisms for the interconversion of the various dioxygen species have been extensively studied. The principal species in acidic solution are shown below.



It is well established that metal ions can profoundly affect both the kinetics and mechanisms of these conversions, often in a catalytic manner. We have used peroxocomplexes of certain metal ions to probe the mechanistic role played by the metal ion. In effect, we start in the middle of the water-oxygen cycle with a well defined system. The redox chemistry of these complexes is compared to that of hydrogen peroxide itself to assess the specific effect of the metal ion on the interconversions. In a few cases we have been able to generate superoxocomplexes and to compare their redox behavior with that of the dioxygen analogue HO_2 .

The early transition metals in their highest oxidation states have been used extensively in these studies. These d^0 ions rapidly form peroxo and superoxo complexes with large formation constants. A critical component of our studies has been to characterize these complexes with respect to formulation, stability constants, rates of formation and dissociation, acid-base properties, and spectra.

A variety of substrates have been examined in the redox studies. Some react with hydrogen peroxide in a non-radical manner, often with oxygen atom transfer from peroxide to the substrate. Other substrates selected show classical Fenton type

chemistry in their reactions with peroxide, with formation of radical intermediates. In most cases the reference reactions with H_2O_2 and/or HO_2 have been previously characterized by other investigators.

Summary of the Most Important Results

Very little was known about the formulation of and particularly the equilibria associated with the peroxocomplexes of interest at the beginning of our project. This data base has been expanded considerably. We may summarize as follows, where the peroxocomplex listed is formed from the indicated metal ion or complex under appropriate experimental conditions: $\text{Ti}(\text{O}_2)^{2+}$ from TiO^{2+} , $\text{Zr}_4(\text{O}_2)_2(\text{OH})_4^{8+}$ from Zr^{4+} , $\text{VO}(\text{O}_2)^+$ from VO_2^+ , $\text{VO}(\text{O}_2)_2^-$ from $\text{VO}(\text{O}_2)^+$, $\text{CrO}(\text{O}_2)_2$ from HCrO_4^- , $\text{MoO}(\text{O}_2)_2$ from HMoO_3^+ , and $\text{WO}(\text{O}_2)_2$ from ? In addition, $\text{UO}_2(\text{O}_2)$ may be formed from UO_2^{2+} , and no peroxocomplexes have been reported for Th^{4+} and ReO_4^- .

We have been able to correlate these observations by means of the following empirical model. We first note that replacement of an oxo group on the precursor by O_2^{2-} from H_2O_2 is an acid independent process, whereas replacement of H_2O or OH^- (not shown in the above formulations) has an inverse acid dependence. Second, we propose that the most stable oxo-peroxo

structure is $\text{MO}(\text{O}_2)_2$, but that this form may not be realized in many cases due to proton requirements and acid-base properties of the precursor.

For example, according to this scheme $\text{Ti}(\text{O}_2)^{2+}$ is readily formed from TiO^{2+} in acidic solution, but to add a second peroxide and/or an oxo group would require a high pH outside the stability region of either oxotitanium(IV) or peroxotitanium(IV). The complex $\text{VO}(\text{O}_2)^+$ is readily formed in acidic solution, but replacement of the second oxo ligand would not be expected. Instead, the stable $\text{VO}(\text{O}_2)_2^-$ species is formed but requires a higher pH, in accord with experiment. The group 6 metal ions form the $\text{MO}(\text{O}_2)_2$ structure directly even in strongly acidic solution, with no evidence for a mono-peroxo complex. $\text{UO}_2(\text{O}_2)$ is formed only in nearly neutral solution, as would be predicted; the reason the oxo groups are not replaced in acidic solution is presumably due to the extremely slow oxygen exchange rate of UO_2^{2+} . As a final illustration, we rationalize the reluctance of ReO_4^- to form a peroxocomplex due to the $[\text{H}^+]^2$ dependence required to form $\text{ReO}(\text{O}_2)_2^+$ and the small tendency of the perrhenate ion to protonate.

Raman spectroscopy has been a valuable tool for determining the solution structure of the peroxocomplexes. The use of oxygen-18 enriched solvent or peroxide has enabled us to assign metal-oxo, metal-peroxo, and peroxo stretching frequencies with

a high degree of certainty.

The rates of oxidation of the peroxocomplexes with most oxidants examined are slower than the corresponding rates with hydrogen peroxide. Relative reduction rates are enormously dependent on the identity of the metal ion. For example, the rates for $\text{Ti}(\text{O}_2)^{2+}$, H_2O_2 , and $\text{MoO}(\text{O}_2)_2$ with a specific reductant stand in the approximate order $10^{-3} : 1 : 10^4$ for a wide variety of substrates. The impressive activation afforded by molybdenum(VI) and tungsten(VI) is strictly catalytic provided hydrogen peroxide is present in excess. Under this condition the metal ion is maintained in the active $\text{MoO}(\text{O}_2)_2$ or $\text{WO}(\text{O}_2)_2$ form due to the rapid formation rate of the oxodiperoxocomplex.

The group 6 metal ions form peroxocomplexes over the entire pH range, although the formulations and equilibria in basic solution have not been established. If the enormous reactivity enhancement observed in acidic solution persists at higher pH, these metal ions should prove to be versatile catalysts in certain practical applications. We have found that all the group 6 $\text{MO}(\text{O}_2)_2$ complexes undergo hydrolysis to form $\text{MO}(\text{OH})(\text{O}_2)_2^-$; the pKa values are 0.8, 1.9, and 3.4 for $\text{M} = \text{W}(\text{VI})$, $\text{Mo}(\text{VI})$, and $\text{Cr}(\text{VI})$, respectively. The hydrolyzed complexes for $\text{Mo}(\text{VI})$ and $\text{W}(\text{VI})$ are about ten times less reactive than the neutral forms, but the relative rates at pH values where the $\text{MO}(\text{OH})(\text{O}_2)_2^-$ species predominates, referenced to H_2O_2 at that pH, remain at $10^4 - 10^5$. These results are encouraging, but the

investigation must be extended into the basic region to assess fully the potential usefulness of these metal ions towards peroxide activation over the entire pH range.

It is important to decipher the mechanism by which these reactions occur. It is reasonable to assume that oxygen transfer from coordinated peroxide to the substrate occurs in many cases; this has been established for H_2O_2 and we are currently extending the studies to selected peroxocomplexes. The probable mechanism would then appear to be either direct attack at the coordinated peroxide by the substrate, or prior coordination of the substrate at the metal ion center followed by oxygen transfer from the adjacent peroxo group. The latter situation appears to apply for reactions with organic substrates in non-coordinating solvents, but does not necessarily hold in aqueous solution. We have recently completed a study of the oxidation of $\text{Co(en)}_2(\text{SCH}_2\text{CH}_2\text{NH}_2)^{2+}$ and $\text{Co(en)}_2(\text{S}\{\text{O}\}\text{CH}_2\text{CH}_2\text{NH}_2)^{2+}$ by $\text{MoO}(\text{O}_2)_2$ and $\text{WO}(\text{O}_2)_2$. These reactions involve oxygen transfer to the coordinated sulfur atom. The idea is that both the charge and structure of the substrate mitigate against coordination to the Mo(VI) or W(VI) center. We find that the relative rates compared to H_2O_2 are again ca. 10^4 , and tentatively conclude that direct attack at the coordinated peroxide occurs.

Oxidation of $\text{Ti}(\text{O}_2)^{2+}$ by Ce(IV) rapidly produces a transient intermediate that we identify as superoxotitanium(IV), although the precise formulation of this species has not been established.

We have studied its redox reactions with a variety of substrates by multi-mixing, stopped-flow procedures and have found that it is somewhat less reactive than its dioxygen analogue, HO_2 . We have initiated studies aimed at forming superoxocomplexes from other peroxocomplexes by similar procedures. It will be fascinating to determine if the redox properties of these complexes show a similar, enormous dependence on the identity of the metal ion as is seen with the corresponding peroxocomplexes.

It may be possible to extend our studies to peroxo and superoxocomplexes of certain nonmetals. For example, peroxoborates are commercially used in some cleansing powders, although their structure in solution is uncertain. A crystal structure of sodium peroxoborate revealed the $\text{B}_2(\text{O}_2)_2(\text{OH})_4^{2-}$ ion; two peroxide ions bridge the borons in the dimeric unit. This species is similar in some respects to the peroxocomplex of zirconium(IV) that we have characterized. The principal point of interest to us is that we may be able to characterize the redox properties of bridging peroxo groups by use of these species; the peroxocomplexes of the d^0 transition metal ions normally show the η^2 , or triangular, structure.

It is possible that our results may provide some insights into the intricate dioxygen chemistry so important in a number of biological systems; however, it is premature at this stage to speculate in a meaningful fashion.

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